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Jon Sertucha, Jacques Lacaze, Rodolfo González-Martínez. Chunky graphite in spheroidal graphite iron: review of recent results and definition of an predicting index. IOP Conference Series: Materials Science and Engineering, 2019, 529, pp.012017. 10.1088/1757-899X/529/1/012017 . hal-02326642

HAL Id: hal-02326642

<https://hal.science/hal-02326642>

Submitted on 22 Oct 2019

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To cite this article: Jon Sertucha *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **529** 012017

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Chunky graphite in spheroidal graphite iron: review of recent results and definition of an predicting index

Jon Sertucha¹, Jacques Lacaze² and Rodolfo González-Martínez¹

¹ Investigación y Desarrollo de Procesos Metalúrgicos, IK4-Azterlan, Aliendalde Auzunea 6, E-48200 Durango (Bizkaia), Spain.

² CIRIMAT, Université de Toulouse, BP 44362, F-31030 Toulouse, France

Jacques.lacaze@ensiacet.fr

Abstract. Graphite degeneracy in heavy-section spheroidal graphite cast irons is mostly associated with the formation of chunky graphite which consists of large eutectic cells with interconnected graphite strings. At low level, appearance of chunky graphite is limited to its non-aesthetic effect on machined surfaces, while at higher level it is detrimental for mechanical properties of the components. Chunky graphite is often related to high silicon levels and too high cerium additions during the spheroidization treatment. The appearance of this defect may be limited by controlled additions of antimony that is thought to tight the excess of cerium, but other impurities and low level elements may have to be considered during melt preparation. This contribution proposes a review of recent results and approaches on chunky graphite appearance, primarily but not exclusively in the case of heavy-section cast irons. Based on this literature review and series of experimental data, a predictive index for evaluating the risk of chunky graphite appearance is proposed. Lines for further research work aimed at a better understanding of graphite degeneracy are finally suggested.

Introduction

The need for melt control before casting of spheroidal graphite cast irons have led for long to look for graphite degeneracy as resulting from melt chemistry. Thielemann developed a trace element evaluation number S_b for assessing the ability of the charge to give well-formed nodules [1]:

$$S_b = 4.4 \cdot w_{Ti} + 2.0 \cdot w_{As} + 2.3 \cdot w_{Sn} + 5.0 \cdot w_{Sb} + 290 \cdot w_{Pb} + 370 \cdot w_{Bi} + 1.6 \cdot w_{Al} \quad (1)$$

where w_i stands for the content in “i” element, expressed in wt.%. When S_b is close to one, the casting should be free from graphite degeneracy while when it is higher than this value addition of rare earth (RE) should be made. This equation is often referenced in the technical literature and sometimes applied to the final cast alloy composition and not to the charge. In his study, Thielemann considered melts cast into samples with thicknesses 8–45 mm. Equation (1) is valid for residual Mg content in the range 0.04–0.08 wt.% while the maximum content in other elements was previously listed [2].

Using a series of casting results from literature, Javaid and Loper [3] suggested to correlate the capability of RE to counteract the detrimental effect of Bi, Pb and Sb to the possible formation of compounds RE_aX_b (with RE=Ce or La and X=Bi, Pb or Sb) such as CeBi, Ce₂Bi or La₃Sb₂ for example. One may write the following balance for the formation of such compound in an iron melt:

$$w_{RE}^{total} - w_{RE}^{limit} = \frac{b \cdot M_X}{a \cdot M_{RE}} \cdot (w_X^{total} - w_X^{limit}) \quad (2)$$

or



$$w_{RE}^{total} = \frac{b \cdot M_X}{a \cdot M_{RE}} \cdot w_X^{total} + \left(w_{RE}^{limit} - \frac{b \cdot M_X}{a \cdot M_{RE}} \cdot w_X^{limit} \right) \quad (3)$$

where w_i^{total} is the amount of element “i” (RE or X) in the liquid cast iron at the time of pouring, w_i^{limit} is the solubility limit of element “i” in liquid iron with respect to precipitation of compound RE_aX_b , and M_i is the molar mass of element “i”. It should be noted that w_i^{limit} may in principle depend on temperature and on the whole iron composition. The statistical analysis performed by Javaid and Loper [3] gave the ratio $\frac{w_{RE}}{w_X}$ – which should be the term $\frac{b \cdot M_X}{a \cdot M_{RE}}$ – equal to 1.1206, 0.840 and 0.914

for Bi, Pb and Sb respectively. However, these authors noted that the scatter of the data was quite large, and the experimental ratio was found to vary in between about 0.5 and 1.5 for all three elements. This scatter is such that any of the compounds of the RE-X systems could have precipitated depending on other melt parameters.

Javaid and Loper [3] then extended the above correlations by expressing that the weight ratio of RE content to the sum of subversive elements should be higher than a critical value for avoiding graphite degeneracy. Considering equation (3), this is certainly an oversimplified approach which could however be efficient. They found that this ratio depends on the effect of other elements, namely P, Si, Mg and Ni, and also on the casting section size. After this seminal work, many authors considered similar ratios for analyzing their results, in particular, in the case of studies on the formation a peculiar graphite degeneracy, the so-called chunky graphite illustrated in figure 1.

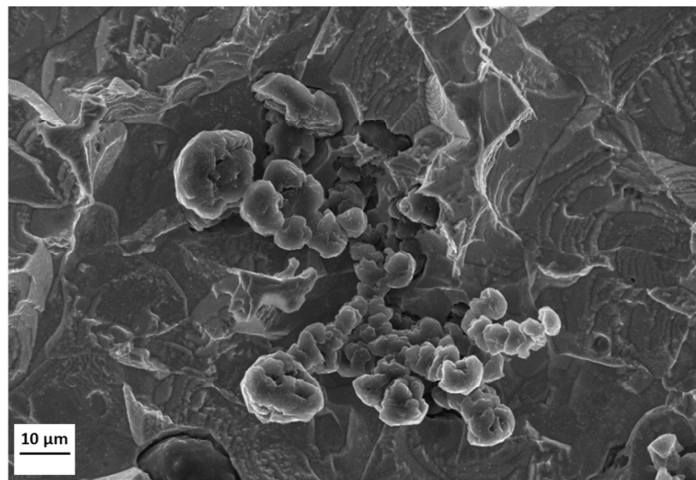


Figure 1 – Chunky graphite strings in a deep-etched ductile iron sample.

While Ce and other rare earths are used to balance the effect of trace elements including Sb (equation 1), Sb is used to counteract the detrimental effect of Ce in heavy-section castings. According to Javaid and Loper [3], the optimum weight ratio of RE to Sb should be 0.916 for RE to counteract the deleterious effect of Sb. This suggests that the optimum ratio of Sb to RE for Sb to counteract the effect of RE in chunky appearance should be 1.095. In fact, Tsumura et al. [4] found that Sb counteracts the effect of Ce when added at a level so that the ratio w_{Sb}/w_{Ce} is higher than 0.8 and Larrañaga et al. [5] confirmed this value.

Following the above lines, Löblich [6] emphasized that elements leading to chunky graphite (Si, Cu, Ni, Ca and Ce) in heavy-section castings may be counteracted by elements known to lead to intercellular graphite (Bi, Pb, Sb and As). Analysing a series of castings containing 2.25 wt.% to 2.70 wt.% silicon, Löblich found that the formation of chunky graphite depends on the silicon content and

on the ratio $\frac{w_{Ce}}{w_{Pb} + w_{Sb} + w_{As}}$. For castings solidifying in about 50 min, Löblich suggested an empirical equation giving the critical silicon content, $w_{Si,limit}$, above which chunky graphite appears. This critical content may be written as:

$$w_{Si,limit} = 2.344 \cdot \left(1 + \frac{0.056}{1.563 - \frac{w_{Ce}}{w_{Pb} + w_{Sb} + w_{As}}} \right) \quad (4)$$

In the absence of cerium and whatever the content in other elements, this equation predicts that no chunky graphite would appear for silicon content lower than 2.43 wt.%. Similarly, a value of 1.563 for the ratio $\frac{w_{Ce}}{w_{Pb} + w_{Sb} + w_{As}}$ would ensure no chunky graphite appears even at high silicon content.

Using values indicated by Löblich, namely w_{Mg} at 0.045 wt.%, w_{Si} at 2.7 wt.% and a casting thickness of 20 cm, equation (4) in Javaid and Loper [3] predicts a critical weight ratio of w_{Ce} over the sum of subversive elements of 1.05 which is reasonably close to Löblich's estimate. Recently, Stets et al. [7] extended the work by Löblich by considering the ratio $(w_{Ce} + w_B + w_{Ca} + w_{Al})$ to $(w_{Bi} + w_{Pb} + w_{Sb} + w_{As})$ for silicon contents lower than 3 wt.%.

Sertucha et al. [8] have conducted a statistical analysis leading to a relation between the extent of the casting section affected by chunky graphite and the composition of the cast irons. The study was based on about 60 melts cast in cubic blocks 300 mm in size with a limited range of silicon contents. The analysis gave a very good correlation coefficient and showed simple and coupled effects of many elements, namely Ce, Cu, La, P, Sb and Sn. However, it appeared difficult to give a physical meaning to these coefficients and this certainly demonstrates the limits of a statistical approach when the number of experiments is not large enough or when hidden factors enter to play.

In a more recent study, González-Martínez et al. [9] investigated the effect of Si on the microstructure of near-eutectic cast irons with various additions of Ce and Sb on a series of 31 alloys cast in Y2 blocks. The silicon content varied in the range 2.29 wt.% to 9.12 wt.%. The area fraction of chunky graphite was measured at the centre of the castings and the ratio of this quantity to the total area fraction of graphite was used as an output parameter. It was first confirmed that silicon promotes chunky graphite as cerium does, and it was also observed that magnesium acts as cerium. Following the type of analysis conducted by Javaid and Loper [3] and expressed with equation (2), it was considered that part of Ce could combine with Sb and analysis of the results showed this happens probably as $CeSb_2$ compound [9]. Limiting the analysis to Si, Ce, Sb and Mg, the following index was proposed:

$$\Omega_{Si} = w_{Si} + 800 \cdot \left(w_{Ce} \cdot \frac{55}{140.1} - 2 \cdot w_{Sb} \cdot \frac{55}{121.8} \right) + 50 \cdot w_{Mg} \cdot \frac{55}{24.3} \quad (5)$$

where $M=55$ stands for the molar mass of the cast iron.

When plotting the area fraction of chunky graphite as function of Ω_{Si} , it was found that this degeneracy appears when the index is higher than about 7 wt.% [9]. In a companion paper [10], a second series of 24 alloys were cast that all contained some Sb to limit chunky graphite appearance. In this second series, the change in silicon content was limited to the domain where maximum mechanical properties are observed, namely 4.84 wt.% to 5.42 wt.% Si. The results of both series are plotted in figure 2-a where it is seen they agree well between each other, indicating again a critical index value of about 7 wt.%.

It appeared of interest to check if this index could apply to previously published results obtained on cubic blocks 300 mm in size [5, 11, 12]. The silicon content of these alloys varied in between 1.92 wt.% and 2.41 wt.% and castings were either or not post-inoculated. The local area fraction of chunky graphite listed in these works is plotted in figure 2-b as a function of Ω_{Si} . It is seen again that chunky graphite appears above a critical value of the index. This critical value is decreased to about 4 wt.% in

agreement with the larger size of the cubic blocks than that of the Y2 keel-blocks corresponding to the case shown in figure 2-a.

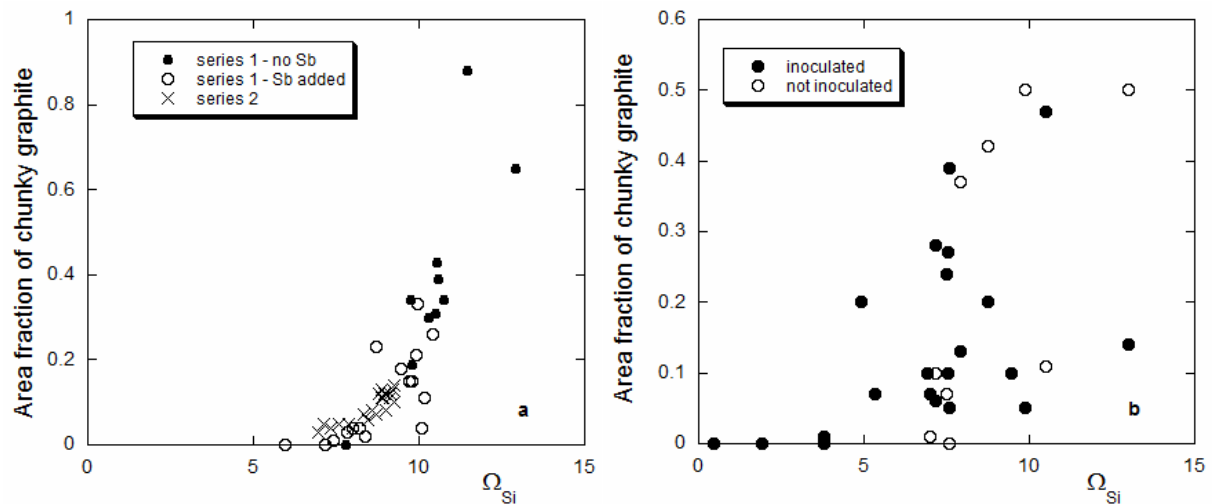


Figure 2 – Fraction of chunky graphite as function of Ω_{Si} for Y2 keel-blocks (a) and 300 mm in size cubic blocks (b).

Discussion

As already mentioned, other elements should be considered and enter in equation (5). This is the case of bismuth whose role on graphite shape in heavy-section ductile iron castings has been recently reviewed by Pokopec et al. [13]. This however needs appropriate experimental data which are not yet available.

Quite recently, Labrecque and Cabanne [14, 15] have reviewed various quality indexes proposed in the literature over several decades. These indexes relate to graphite degeneracy, pearlite promoters or, else, low temperature brittleness. However, none of them are able to account for the fact that there may be an optimum addition of counteracting elements as was stressed by Gagné and Argo [16] when studying the role of Sn and Sb on the formation of chunky graphite. From the present study, it appears that such an optimum should be considered also for Mg and Ce (or more generally RE). It would thus be highly helpful to develop a basic knowledge on the thermodynamic interactions in real cast irons as well as a large database dedicated to a statistical analysis of the cross-effects of low level elements.

Finally, it is worth stressing that the growth mechanism of chunky graphite is far from being understood. As a matter of fact, it was observed that the alloy with 9 wt.% Si in the studied series [9] presented little chunky graphite, at most a fraction of 0.17. This graphite is illustrated in figure 3. This low graphite degeneracy is in contrast with the high Ω_{Si} value for this alloy. This certainly has to do with the fact that this alloy solidified with ferrite as iron-rich phase and not austenite in agreement with the assessed Fe-C-Si phase diagram [17]. As chunky graphite grows as a coupled eutectic with the iron-rich matrix, a possible schematic of the solidification front has been proposed previously for the case when the iron-rich phase is austenite [18]. This schematic is shown in figure 4 where growth of graphite at the interface with the liquid is assumed to follow a 2D nucleation growth model [19]. In figure 4, the value of the surface tension between liquid and graphite, $\gamma^{l/G}$, is such that it counterbalances exactly the sum S of the austenite/graphite, $\gamma^{\alpha/G}$, and austenite/liquid, $\gamma^{\alpha/l}$, surface tensions. As it is admitted that the surface tension between ferrite and liquid, $\gamma^{\alpha/l}$, is lower than $\gamma^{\alpha/l}$ [20], the forces will not be any more balanced at the three-phase junction making chunky graphite growth more difficult when the iron-rich phase is ferrite.

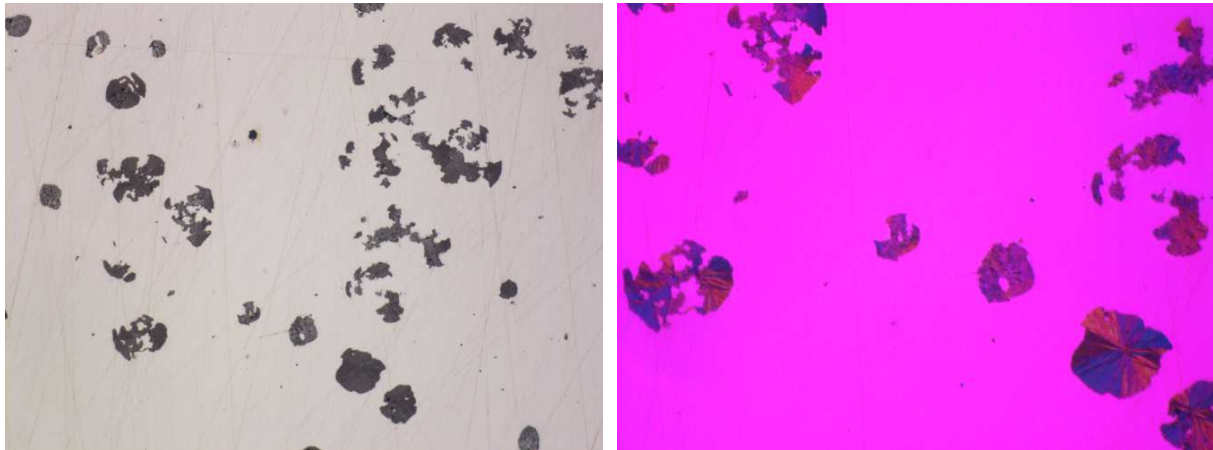


Figure 3 – Light optical micrograph of graphite in the 9 wt.% Si alloy: bright field image (a) and polarized light image of part of the area in a (b)

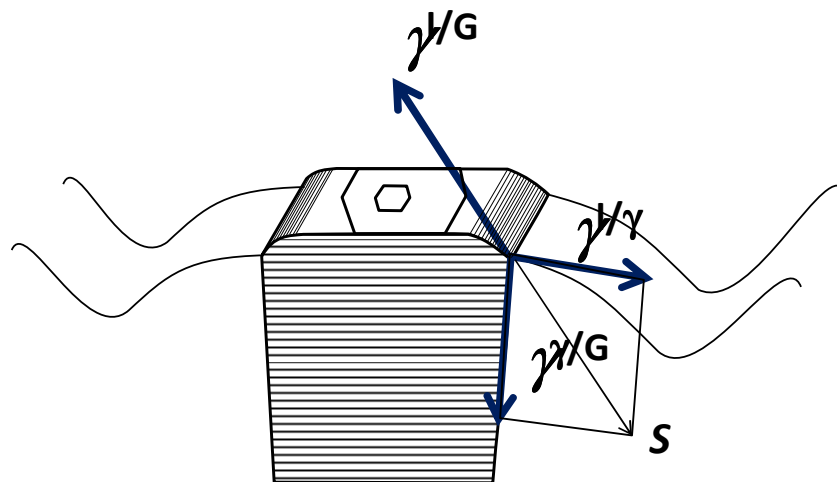


Figure 4 – Schematic of the coupled eutectic solidification front of chunky graphite and austenite

Conclusion

While it has been known for long that chunky graphite in spheroidal graphite cast irons depends also on melt composition, very few quantitative studies are available. More important than that, it appears impossible to compare the results of these rare studies as full details for such a comparison are not available. The index proposed here to characterize the propensity of a melt to chunky graphite degeneracy has been developed on the basis of more than 50 melts cast in Y2-blocks. A tentative extension to other cooling conditions has been shown which would need being better substantiated.

Interestingly enough, growth of chunky graphite is certainly not definitely understood though figure 4 suggests one mechanism. It is evident that clarifying this mechanism would help finding ways to avoid its appearance.

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